METHOD FOR REGENERATION OF PERFORMANCE
IN A FUEL CELL

Field of the Invention

5   This invention relates to the regeneration of performance of a fuel cell and stack thereof, and more particularly to methods for regeneration of a direct feed fuel cell, such as a direct methanol fuel cell (DMFC), and stack thereof.

Background of the Invention

10   Solid polymer electrolyte fuel cells employ a membrane comprising a solid polymer electrolyte disposed between two porous electron and proton conductive electrodes, the anode and the cathode compartments. The anode and cathode compartments include catalyst layers, gas diffusion layers, and electron conductive flow field plates. Fuel is fed into the anode flow field,
15 diffusing onto the porous catalyst layer, and is oxidized to produce electrons, protons, and CO_2 as a by product when methanol aqueous solution is used as fuel. The polymer electrolyte membrane is proton conductive allowing the protons to migrate towards the cathode. At the same time, oxidant is fed into the cathode compartment wherein the oxidant diffuses onto the porous
20 cathode catalyst layer and reacts with the protons and electrons, producing water as a by-product. The electrons travel from the anode to the cathode through an external circuit, thus producing the desired electrical power.

      In stationary applications, fuel cell systems may be required to operate continuously for a period of time. However, in portable or traction power
25 applications, fuel cell systems may be subjected to frequent start-up and shut down cycles. In either case, the fuel cell is expected to provide a reliable power output under specified conditions. Unfortunately, the power output of the fuel cell decreases with operation time under the same operating conditions. For example, fuel cell or stack voltage decays with time at a given
30 operating current density, or vice versa. This cell or stack voltage decay obviously affects overall fuel cell efficiency. More importantly, it may limit fuel cell applications. Therefore, the recovery of fuel cell performance after a period of operation or bringing a fuel cell to a starting up condition after a period of operation is very important in a fuel cell application.

A need exists for a method for regeneration of performance of a fuel cell, typically a direct feed fuel cell, after a period of operation and a method for start up of a fuel cell system after a period of operation.

Summary of the Invention

5   In a first aspect, the invention provides a process for improved performance in at least one fuel cell comprising a cathode, an anode, an anode chamber, a cathode chamber, a fuel comprising an anolyte that flows through the cell, and a catholyte gas, wherein the fuel cell is connected to an external load, and wherein the process comprises:

10   (a1) taking the load off the fuel cell; and either

(a2) cycling between a minimum voltage, which is defined as about 0.1 to about 30% of the maximum voltage (wherein maximum voltage is defined as the voltage for cell/stack when there is substantially no load being drawn from a healthy fuel cell, i.e. a cell that does not require

15   regeneration), and at least about 50% of the maximum voltage, typically about 60 to about 90% of the maximum voltage, and more typically about 90 to about 100% of the maximum voltage, until a maximum current is reached. , or

(a3) cycling between a minimum load, which is defined as about 0 to

20   about 5% of the maximum load, and at least about 50% of the maximum load, typically about 60 to about 90% of the maximum load, and more typically about 90 to about 100% of the maximum load, until a maximum voltage is reached.

In the first aspect, the invention further provides a process wherein

25   before step (a2) or (a3), the process further comprises:

(b) clearing the fuel cell of any liquid present therein to achieve a resistance of at least about 10% higher, more typically at least about 20% higher, and still more typically about 100 to about 500% higher, than the value before clearing the cell of any liquid; and

30   (c) starting the flow of anolyte through the fuel cell.

Brief Description of the Drawings

Figure 1 is a schematic illustration of a single cell assembly.

Figure 2 is a schematic illustration of a typical DMFC test station.

Figure 2A illustrates the regeneration of long term performance of a DMFC with voltage cycling.

Figure 3 is a graph showing the effect of room temperature voltage cycling on the performance of a DMFC.

5   Figure 4 is a graph showing the optimum IV curve from Figure 3 after voltage cycling, and the IV curve for said cell after 80 °C treatment.

Figure 5 is a graph showing the cell voltage of a DMFC and its AC Impedence varying with time during a regeneration procedure.

Figure 6 illustrates the advantages and effectiveness of the regeneration

10   procedure on the long-term performance of a DMFC.

Figure 7 is a graph showing stack performance regeneration by a combination of purge and toggle operations.

Detailed Description of the Invention

A process is provided for improved performance in at least one fuel cell

15   comprising a cathode, an anode, a fuel comprising an anolyte that flows through the cell, and a catholyte gas, wherein the fuel cell is connected to an external load, and wherein the process comprises cycling between a minimum voltage, which is defined as about 0.1 to about 30% of the maximum voltage (wherein maximum voltage is defined as the voltage for cell/stack when there

20   is substantially no load being drawn from a healthy fuel cell, i.e. a cell that does not require regeneration), and at least about 50% of the maximum voltage, typically about 60 to about 90% of the maximum voltage, and more typically about 90 to about 100% of the maximum voltage, until a maximum current is reached. Alternately, cycling between a minimum load, which is

25   defined as about 0 to about 5% of the maximum load, and at least about 50% of the maximum load, typically about 60 to about 90% of the maximum load, and more typically about 90 to about 100% of the maximum load, until a maximum voltage is reached.

The fuel cell may be a direct feed fuel cell, wherein the fuel is in the

30   liquid or vapor phase. Some suitable fuels include alcohols such as methanol and ethanol; ethers such as diethyl ether, etc.

For the purpose of this application, the term "anode" is used to describe the component of the fuel cell comprising the anode flow field plate, anode gas diffusion layer and anode catalyst layer. The term "cathode" is used to describe the component of the fuel cell comprising the cathode flow

5   field plate, cathode gas diffusion layer and cathode catalyst layer.

The term "stack" refers to a fuel cell stack comprising a series of fuel cells functioning in tandem electrically.

Fuel Cell:

10   Figure 1 schematically illustrates a single cell assembly. As shown in Figure 1, the MEA (30) comprised a catalyst coated membrane, (CCM) (10) sandwiched between two sheets of the gas diffusion backing, (GDB) (13). The anode and cathode gas diffusion backings (13) may comprise carbon paper or cloth and typically a fluorinated polymeric surface-treating agent, although

15   other surface treatments may be used. A microporous layer or layers such as those manufactured by E-Tek Inc., Natick, MA may also be present in the cathode gas diffusion backing wherein the microporous layer may typically be disposed toward the cathode catalyst. A glass fiber reinforced silicone rubber gasket (19), for example (Furan - Type 1007, obtained from Stockwell Rubber

20   Company), cut to shape to cover the exposed area of the membrane of the CCM, may be placed on either side of the CCM/GDB assembly (taking care to avoid overlapping of the GDB and the gasket material). The entire sandwich assembly may be assembled between the anode and cathode flow field graphite plates (21). One such 25cm^2 standard single cell assembly may

25   be obtained from Fuel Cell Technologies Inc., Los Alamos, NM. The cell shown in Figure 1 may also be equipped with anode inlet (14), anode outlet (15), catholyte gas inlet (16), catholyte gas outlet (17), aluminum end blocks (18), tied together with tie rods (not shown), electrically insulating layer, (20), and gold plated current collectors, (22). Bolts on the outer plates (not shown)

30   of the single cell assembly may be provided and tightened with a torque wrench to a torgue of 1.5 ft. lb.

A characteristic of liquid feed fuel cells, and in particular direct methanol fuel cells, using a solid polymer electrolyte membrane is that the liquid feed, e.g. aqueous methanol solution, is directly used as fuel. Aqueous

methanol solution is fed into the anode of the fuel cell. Air or oxygen is fed into the cathode of the fuel cell. In a DMFC operation, both methanol and water will transport through the proton conductive membrane from the anode to the cathode by both diffusion and osmotic drag. In addition to water

5   crossover, water is also generated at the cathode as a by-product. Therefore, the cathode electrode could be flooded with water if the water removal rate is smaller than the water generation rate at the cathode.

It is desirable to have a stable power output at given fuel cell operating conditions. Unfortunately, fuel cell power output decays with operating time

10   while other operating conditions are kept the same. Because of this voltage decay, a DMFC stack may not be able to provide a desirable power output after a period of operation. Performance decay is an important issue in a DMFC application.

The factors causing the voltage decay may be very complex and some

15   factors are outlined below. It may be one of the following factors or the combination of the following factors:

(1). Catalyst degradation at the anode;

(2). Catalyst degradation at the cathode;

(3). Effect of impurities from the feeds and from the materials of fuel

20   cell structure;

(4). Deterioration of materials used for the stack leading to increase in resistance;

(5). Accumulation of water at the cathode electrode;

(6). Accumulation of CO_2 at the anode electrode and the diffusion layer;

25   (7). Accumulation of CO at the anode electrode;

(8). Other causes;

(9). Combination of the factors above.

Factors (1) to (4) may cause physical damage to the fuel cell stack,

30   that is permanent decay of the fuel cell stack, whereas factors (5) to (7) are the effects caused by the operating conditions for a given fuel cell system, that result in a temporary decay. This invention discloses a method to recover this temporary decay for given fuel cells and stack designs and operating conditions.

Process for Regeneration:

The following steps may be performed to regenerate a fuel cell:

To start with the cell was brought to an open circuit, i.e., the load on the

5   cell was taken out. For example, a cell that has been operated for a period of
time may have a voltage or power output about 5% lower than the desired
value. The cell needing regeneration was then cycled between a minimum
voltage and at least about 50 % of the maximum voltage, typically about 60 to
about 90% of the maximum voltage, and more typically about 90 to about

10   100% of the maximum voltage, a number of times until a maximum current
was reached, e.g. about 1 to about 20 times, more typically about 6 to about
10 times, with the anode and cathode flow continuing. For example, cycling
may occur between the open circuit voltage (OCV) and 0.2V. Minimum
voltage is defined, as about 0.1 to about 30% of the maximum voltage,

15   wherein maximum voltage is defined as the voltage for cell/stack when there
is no load being drawn.

Alternately, the load on the fuel cell may be cycled between a minimum
load and at least about 50% of the maximum load, typically about 60 to about
90% of the maximum load, and more typically about 90 to about 100% of the

20   maximum load, until a maximum voltage is reached. For example, this
includes cycling between no current being drawn from the cell/stack and the
rated maximum current density of the cell/stack, until a maximum voltage is
reached. Cycling may occur about 1 to about 20 times, more typically about
6 to about about 10 times. Minimum load is defined as about 0 to about 5% of

25   the maximum load. The load was again applied to the cell and the voltage
monitored with time.

In a second embodiment, the following steps may be performed to
regenerate a fuel cell: To start with the cell was brought to an open circuit, i.e.,
the load on the cell was taken out. For example, a cell may have a voltage or

30   power output about 5% lower than the desired value. Optionally, an
impedance meter may be connected across a cell needing regeneration
wherein the drop in power output was dependent on the end use application.
This was done under load (at the desired current density) to measure the cell
resistance (both when on load and when on open circuit). The flow of anolyte

such as a methanol solution, an ethanol solution, etc., was stopped. The anolyte temperature was dependent on the power output and other operating conditions for the cell. The catholyte gas, e.g. air, flow through the cell was continued throughout the process. Optionally, the flow of catholyte gas may

5   be interrupted. The resistance of the cell may be closely monitored. After a certain period of time, the cell resistance slowly crept up and increased to very high values. Clearing the fuel cell of any liquid present therein results in a resistance of at least about 10% higher, more typically at least about 20% higher, and still more typically about 100 to about 500% higher than the value

10   before clearing the cell of any liquid. Optionally, at this stage, the anode side was purged with air, nitrogen or exhaust from the cathode compartment. The cell was left under these conditions for a given period of time and then the anolyte flow through the cell was turned on, wherein the anolyte was at the desired temperature. Optionally, the desired temperature may be achieved

15   using a pre-heater. The resistance of the cell may be monitored and the cell was cycled between no load and full load, for example, between open circuit voltage (OCV) and 0.2V, until the resistance dropped to values similar to those at the start of the regeneration process. The cell was then set at the given load and operation of the cell was resumed.

20   Following such a sequence of steps results in considerable improvement in performance of the cell after regeneration, in terms of both the power output and the rate of drop in voltage with time. Improved performance in the form of cell activation may also be further achieved using the voltage cycling steps until a maximum current was achieved.

25   In a separate embodiment, in addition to the above steps, the cathode was purged using air or nitrogen at open circuit condition of the stack after the stack was operated for a period of time. The performance of cell/stack can be further recovered by purging the cathode compartment when the cell/stack is at open circuit and anode fuel feed is turned off. The cathode chamber is

30   purged with air, nitrogen or exhaust from the cathode compartment for at least about 10 seconds, typically about 30 seconds to about 5 minutes.

       In addition to the cycling steps described above, a more effective method to recover the temporary decay of cell/stack performance after a period of operation was to turn off the load of the cell/stack; turn off the fuel

supply to the anode; and purge the anode compartment using the same air
stream that was used for the cathode feeding. Nitrogen or the exhaust from
the cathode compartment may also be used for the purging step. After
purging the anode for a short period of time, the cathode compartment was

5   purged using the same air steam for the cathode feeding or nitrogen. After
the purging operation, the cell/stack was subjected to normal operation. It
was found that the temporary decay of the cell/stack was fully recovered. In
the above method, the cell/stack performance may be fully recovered by
purging the anode, without the cathode compartment being purged.

10 The recovery of cell/stack performance was independent of oxygen
concentration when purging the anode, i.e., using either air, nitrogen or the
exhaust from the cathode compartment can obtain the same result of
cell/stack performance recovery.

In a DMFC application, any purging required is a parasitic energy loss.

15 Therefore, the shorter the duration of purging, the better. Based on the stack
design used for this invention, a typical time range for anode purging is about
0.01 to about 30 minutes, typically about 0.1 to about 30 minutes. A more
typical time range is 1 to 15 minutes. A typical time range for the cathode
purge is less than 5 minutes. A typical purging temperature is the cell/stack

20 operating temperature. The cell/stack temperature could decrease during the
purge operation.

In a multiple stack application, in order to maintain continuous power
output, regeneration operations can be scheduled so that some stacks are in
normal operation and others are being regenerated using the method above.

25 The regeneration procedures described above may be performed right
after the stack is shut down or at the start up period. Because the purging
operation is more effective at relatively high temperatures, it is preferred to
perform the regeneration operations at the shut down process.

30 <u>Examples</u>

<u>CCM Preparation Procedure:</u>

The cathode catalyst dispersion was prepared in a Eiger® bead mill,
manufactured by (Eiger Machinery Inc., Greybrlake, IL 60030), containing 80

ml 1.0-1.25 zirconia grinding media. 13.5 grams platinum black catalyst powder (catalyst grade (obtained from Colonial Metals, Elkton, MD) and 42.8 grams of the 3.5wt% Nafion® solution (the polymer resin used in such a solution was typically of 930EW polymer and was in the sulfonyl fluoride form)

5   were mixed and charged into the mill and dispersed for 2 hours. Material was withdrawn from the mill and particle size measured. The ink was tested to ensure that the particle size was under 1 micron and the % solids in the range 13.56-13.8. The catalyst decal was prepared by drawing down the catalyst ink to a dimension of 5 cm x 5 cm (to give a total area of 25 cm^2) on a 10cm x

10   10cm piece of 3 mil thick Kapton® polyimide film manufactured by E.I. du Pont de Nemours & Co., Wilmington, DE. A wet coating thickness of 5 mil (125 microns) typically resulted in a catalyst loading of 4 to 5 $mgPt/cm^2$ in the final CCM. Anode decals were prepared using a procedure similar to that described above, except that in the catalyst dispersion, the platinum black

15   catalyst was replaced by platinum/ruthenium black catalyst powder (obtained from Johnson Mathey Inc.). The CCM is prepared by a decal transfer method. A piece of wet Nafion® N117 membrane (4" x 4") in the H^+ form, manufactured by DuPont, was used for CCM preparation. The membrane was sandwiched between two anode and cathode catalyst coated decals. Care was taken to

20   ensure that the coatings on the two decals were registered with each other and were positioned facing the membrane. The entire assembly was introduced between two pre-heated (to 145C) 8" x 8" plates of a hydraulic press and the plates of the press were brought together without wasting much time until a pressure of 5000 lbs. is reached. The sandwich assembly was

25   kept under pressure for ~2 mins. and then the press was cooled for ~2 mins. (viz., till it reached a temperature of <60°C) under same pressure. Then the assembly was removed from the press and the Kapton® films were slowly peeled off from the top of the membrane showing that the catalyst coating had been transferred to the membrane. The CCM was immersed in a tray of water

30   to ensure that the membrane was completely wet, and carefully transferred to a zipper bag for storage and future use.

Chemical treatment of CCMs

       The CCMs were chemically treated in order to convert the ionomer in the catalyst layer from the -SO_2F form to the –SO_3H form. This requires a

5   hydrolysis treatment followed by an acid exchange procedure. The hydrolysis of the CCMs was carried out in a 30-wt % NaOH solution at 80°C for 30min. The CCM's were placed between Teflon® mesh, manufactured by DuPont, and placed in the solution. The solution was stirred to assure uniform hydrolyses. After 30 minutes in the bath, the CCM's were removed and

10   rinsed completely with fresh DI water to remove all the NaOH.

       Acid exchange of the CCMs that were hydrolyzed in the previous step was done in 15-wt % Nitric Acid Solution at a bath temperature of 65°C for 45 minutes. The solution was stirred to assure uniform acid exchange. This procedure was repeated in a second bath containing 15-wt % Nitric acid

15   solution at 65°C and for 45 minutes.

       The CCMs were then rinsed in flowing DI water for 15 minutes at room temperature to ensure removal of all the residual acid. They were then packaged wet and labeled. The CCM (10) comprised a Nafion® perfluorinated ion exchange membrane (11); and electrodes (12), prepared

20   from a platinum catalyst and Nafion® binder on the anode side, and a platinum/ruthenium catalyst and Nafion® binder on the cathode side.

Fuel Cell Performance Evaluation Procedure:

       Figure 1 schematically illustrates a single cell assembly.   Fuel

25   cell test measurements were made employing a single cell test assembly obtained from Fuel Cell Technologies Inc, New Mexico. As shown in Figure 1, the MEA (30) comprised the CCM (10) sandwiched between two sheets of the GDB (13) (taking care to ensure that the GDB covered the catalyst coated area on the CCM). The anode gas diffusion backing (13) comprised carbon

30   cloth and a fluorinated polymeric surface-treating agent. The cathode diffusion backing comprised an ELAT with a single microporous layer from E-Tek Inc., Natick, MA. The microporous layer was disposed toward the cathode catalyst. A glass fiber reinforced silicone rubber gasket (19) (Furan® - Type

1007, obtained from Stockwell Rubber Company, Philadelphia, PA), cut to shape to cover the exposed area of the membrane of the CCM, was placed on either side of the CCM/GDB assembly (taking care to avoid overlapping of the GDB and the gasket material). The entire sandwich assembly was

5   assembled between the anode and cathode flow field graphite plates (21) of a 25cm^2 standard single cell assembly (obtained from Fuel Cell Technologies Inc., Los Alamos, NM). The test assembly shown in Figure 1 was also equipped with anode inlet (14), anode outlet (15), catholyte gas inlet (16), catholyte gas outlet (17), aluminum end blocks (18), tied together with tie rods

10   (not shown), electrically insulating layer, (20), and gold plated current collectors, (22). The bolts on the outer plates (not shown) of the single cell assembly were tightened with a torque wrench to a force of 1.5 ft. lb.

        The single cell assembly was then connected to the fuel cell test station (a schematic of which is shown in the Figure 2. The components in a test

15   station include a supply of air for use as catholyte gas (41); a load box to regulate the power output from the fuel cell (42); a MeOH solution tank to hold the feed anolyte solution (43); a heater to pre-heat the MeOH solution before it enters the fuel cell (44); a liquid pump to feed the anolyte solution to the fuel cell at the desired flow rate (45); a condenser to cool the anolyte exit from the

20   cell from the cell temperature to room temperature (46) and a collection bottle to collect the spent anolyte solution (47)

        With the cell at room temperature, 1M MeOH solution and air were introduced into the anode and cathode compartments through inlets (14) and (16) of the cell at flow rates of 25cc/min and 3 SLPM (standard liters per

25   minute), respectively. The gas streams were humidified with water vapor before they entered the cell. The temperature of the single cell was slowly raised till it reached 80°C. Typically, a current-voltage polarization curve was recorded. This comprised of recording the current output from the cell as the voltage was stepped down in 50 mV steps starting from the open circuit

30   voltage (OCV) down to 0.15 V and back up to OCV. The voltage was held constant in each step for 20sec to allow for the current output from the cell to stabilize.

Example 1:

A standard 25cm^2 CCM prepared as described above was assembled in a cell. The cell was heated to a temperature of 60°C. 1M MeOH solution was used as the anolyte and a flow rate of 2ml/min. Air was used as the

5   oxidant at 100sccm. The cell was tested at a constant load of 50mA/cm2 and the cell voltage was monitored with time. After 480 mins of testing under these conditions, the cell voltage had dropped by more than 15% from the initial value (dropped from ~0.4V to 0.33V). At this point, the load on the cell was taken out and cell was cycled between OCV and 0.2V eight times with

10   the anode and cathode flows continuing. After this voltage cycling, the load (of 50mA/cm2) was again applied to the cell and the voltage was monitored with time. The results are presented in Figure 2A. Immediately following the voltage cycling sequence, the cell voltage (under the constant load) returned to 0.4V (the value at the beginning of the test) proving the effectiveness of the

15   voltage cycling sequence in regenerating the lost fuel cell performance.

Example 2:

A standard 25cm^2 CCM prepared as described above was loaded in a cell and cycled at room temperature (RT) between 0.905V and 0.005V at a

20   rate of 20mV/sec (with air at 3 SLPM and 1M MeOH flow of 25cc/min). The cycling was to decrease the voltage from 0.905 to 0.005V and back to 0.905V at the stated rate. A total of 10 cycles was performed. Then a standard IV curve was recorded on the sample at RT (0.8V to 0.1V and back to 0.8v in 50mV steps and 20 sec at each step). The temperature of the cell was then

25   raised to 80°C where a couple of standard IV curves were recorded with air and oxygen. The cell was then cooled to RT and then again an IV curve was recorded under the same conditions as before.

There was a definite improvement in performance upon RT cycling (see Figure 3) up to 7 cycles. Then the performance remained constant.

30   An attempt was made to verify if high temperature treatment (cycling) of the sample would improve the performance further. But the data indicates that it was not the case. There was no further activation on cycling at high temperature. Results are shown in Figure 4.

This experiment demonstrated that room temperature activation of fuel cells was achieved by cycling between a maximum voltage and minimum voltage drawn from the fuel cell until a maximum current was reached.

5 **Example 3:**

This example shows the regeneration of a fuel cell using the following steps: An impedence meter was connected across a cell needing regeneration and identified in the graph as EO48. The cell had a voltage or power output about 15% lower than the desired value. This was done under

10 load at 200 mA/cm^2 to measure the cell resistance (both when on load and when on open circuit). The cell resistance was found to be 6.9 mOhm. This was followed by the cell being brought to an open circuit, i.e., the load on the cell was taken out. Next, the flow of anolyte [1M MeOH solution] through the cell was stopped. The flow of catholyte gas, which was air, through the cell

15 was continued throughout the process and the resistance of the cell was closely monitored. After a certain period of time the cell resistance slowly crept up and increased to 55 mOhm and the cell was left under these conditions for 60 seconds. Next, the anolyte [1M MeOH solution] flow through the cell was turned on at a rate 0f 25 ml/min. The resistance of the cell was

20 monitored and the cell was cycled between open circuit voltage (no load) and 0.2V until the resistance dropped to 7.2 mOhm. The cell was then set at 200mA/cm^2 load to return it to normal operation. The results are summarized in Figure 5.

The process steps outlined above resulted in considerable

25 improvement in performance of the cell, after regeneration as compared to that before regeneration, both in terms of the power output and the rate of drop in voltage with time. This process was repeated after every 36 hours of operation of the under load (of 200mA/cm2) to regenerate the cell.

30 **Example 4:**

A comparison was made between the performance of two samples that were prepared as described in the CCM Preparation Procedure, one without the regeneration treatment and the other with. The results are shown in Figure 6. Plotted on the graph was the two-hour average power output that

13

was taken after one hour of operation at load after each regeneration step. This was shown as a percentage of the average initial power output as a function of the time.

The first curve identified as EJ24 was on a cell wherein the

5   regeneration treatment was not used. After each break, the sample was restarted and set to the given experimental conditions. The anolyte and catholyte gas flows were not changed during the break period. The second curve identified as ELO1 was run for ~900hrs under conditions similar to EJ24.   But at this point, the regeneration treatment described in Example 3

10   was adopted at each break (i.e., starving the cell of anolyte during the break period at the cell temperature of 80 °C. Such a treatment resulted in a significant reversal of the behavior where the power output increased significantly.

15   **Example 5:**

Example 3 was repeated with the following exceptions: The sample to be tested was EO43. This sample was subjected to the previously outlined regeneration treatment as described in Example 3 right from the start instead of after 900 hours of operation. Care was taken to ensure that the voltage (at

20   a constant load of $0.2A/cm^2$) did not drop by more than 20% (of the initial value) at any point of time.   As soon as the cell voltage dropped by about 20%, the cell was subjected to the regeneration treatment. The performance of the cell rebounded back significantly and overall performance of the cells was relatively much better than the previous cells (EJ24 and EL01 in Figure

25   6).

Example 6:

A DMFC stack comprising 6-fuel cells was used in this example. Each fuel cell included electrodes with active area of 100 cm^2. The anode catalyst was Pt/Ru alloy, 4 mg/cm^2, and the cathode catalyst was Pt, 4 mg/cm^2. Nafion® 117 (DuPont) was used as proton conductive membrane and electron conductive carbon cloth was used as the diffusion layers for both the anode and cathode. Conductive plates with multiple flow channels were used as current collecting plates for the anode and cathode flow field plates (21).

The DMFC stack was operated at the following conditions in this example:

Methanol solution feed rate:	300 cc/min
Methanol concentration:	3.2 wt%
Air feed rate:	15 SLPM
Stack temperature:	80°C
Current density:	0.2A/cm^2

The stack was operated with the above conditions and at the current density of 0.2A/cm^2 for 3 hours. Then, the load was turned off and fuel feed to the anode was also turned off. The anode and cathode of stack were purged using air with feed rate of 30 SLPM for 5 minutes each. After the purge, the stack was operated with on/off load for a period of time. The stack was operated off load for 20 seconds and at 1.2V for 1 minute and the cycle was repeated 15 times (toggle operation). After operation at 0.2A/cm^2 for 2 hrs and 50 minutes, the stack was subjected to the purge and toggle operations. The performance of the stack was recovered and was better than the starting point where purge and toggle operation were not performed. The results of above operation are shown in Figure 7. Curve 1 represents the voltage at the start and after the toggle operation in the fuel cell regeneration process. When the stack was operated at 0.2A/cm^2 for 3 hrs, the stack was purged and toggled as described above and its operation was continued at 0.2A/cm2.

The performance of the stack was recovered after the regeneration operation. Curve 2 represents the voltage changes between the fuel cell stack that was not purged at startup and after the purge and the toggle operations.